

CATALYTIC ACTIVITY OF OXIDIZED (COMBUSTED) OIL SHALE FOR REMOVAL OF NITROGEN OXIDES WITH AMMONIA AS A REDUCTANT IN COMBUSTION GAS STREAMS

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ABSTRACT

Oxidized oil shale from the combustor in the LLNL hot recycle solids oil shale retorting process has been studied as a catalyst for removing nitrogen oxides from laboratory gas streams using NH₃ as a reductant. Combusted Green River oil shale heated at 10°C/min in an Ar/O₂/NO/NH₃ mixture (~ 93%/6%/2000 ppm/4000 ppm) with a gas residence time of ~ 0.6 sec exhibited NO removal between 250 and 500°C, with maximum removal of 70% at ~ 400°C.

Under isothermal conditions with the same gas mixture, the maximum NO removal was found to be ~ 64%. When CO₂ was added to the gas mixture at ~ 8%, the NO removal dropped to ~ 50%. However, increasing the gas residence time to ~ 1.2 sec, increased NO removal to 63%.

These results are not based on optimized process conditions, but indicate oxidized (combusted) oil shale is an effective catalyst for NO removal from combustion gas streams using NH₃ as the reductant.

INTRODUCTION

Green River oil shale contains 10+ wt % organic material. Pyrolyzed for a few minutes at 500°C, this shale releases ~ 80% of the organic matter as oil vapors and non-condensable gases. The balance of this organic material is left in the retorted shale as a solid (char). Efficient oil shale processes, such as the LLNL hot recycle solids (HRS) retort process, burn this char to heat the raw feed shale (1).

The ratio of nitrogen to organic carbon in Colorado Oil shale and retorted shale is higher than in most other fossil fuels. As a result, the concentration of NO_x and NH₃ in the combustion flue gas of the HRS process are high. Under normal HRS pilot plant operations, the combustion flue gas contains ~ 5% O₂, ~ 50 ppm NH₃, and ~ 500 ppm NO. This NO emission level is high by a factor of ~ two for current coal combustion standards in the U. S. (2). Under oxygen starved (fuel rich) combustion, the concentration of NO falls to ~ 250 ppm.

At present, a practical way of lowering NO_x emissions in industrial boilers employs selective catalytic reduction (SCR) using NH₃ at ~ 300°C (3). Non catalytic reduction of NO_x by NH₃ at about 950°C (thermal denox) is also practiced (4).

We are investigating factors which influence emissions of NH_3 and NO during oxidation of retorted shale. We have reported on the oxidation and thermal decomposition of NH_3 , as well as utilizing retorted oil shale for NO reduction (5). Here we report the use of NH_3 as a reducing agent for NO over oxidized (combusted) oil shale.

EXPERIMENTAL

Experiments were performed at constant heating rates or isothermally at ambient-pressure in a 2.5-cm diameter, 50-cm long silica glass tube mounted vertically in an electric furnace. The thermal center of the tube was filled over a length of ~ 8 cm with the material being examined. Bed materials were either oxidized (combusted) Green River oil shale (22 gal/ton) or porous white firebrick. The shale bed used in the constant heating rate experiments was prepared by burning shale at temperatures as high as 850°C in air which assured that a significant fraction of the calcite (CaCO_3) in the shale was decomposed to lime (CaO), and no organic carbon remained. The shale used in the isothermal experiments was taken from the HRS pilot plant where combustion was at temperatures below 750°C , resulting in little CaCO_3 decomposition. This shale sample contained ~ 0.3 wt % unburnt char, typical of processed shale. Both shale samples weighed 27 g and had a particle size range from 1.4 to 2.8 mm. The bed porosity was $\sim 40\%$, and the porosity of the individual shale grains was $\sim 25\%$.

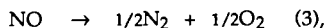
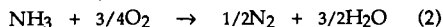
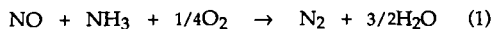
Temperature of the bed was measured with a thermocouple located at the center of the bed. The gas mixtures were passed down flow at a rate of either ~ 1 or ~ 0.5 L/min. At the 1 L/min rate, the transit or contact time between the flowing gas and shale at 300°C was about 0.6 sec. The gas compositions were constructed to simulate an idealized HRS combustor output, with and without CO_2 . Ar was selected as the carrier gas to facilitate detection of product N_2 .

Analysis of NH_3 , NO , NO_2 , N_2 , H_2 , O_2 , H_2O , and Ar was by an EXTREL Questor model mass spectrometer. Calibration for all gases except H_2O was accomplished by means of commercial gas standards and air. The mass spectrometer was connected to the reactor by a 304 SS line heated at 150°C . Data was taken every 10 to 15 sec. Because both N_2O and CO_2 have m/z 44, they can not be differentiated in the mass spectrometer. In the cases where CO_2 was absent in the inlet gas, m/z 44 was considered due mainly to N_2O . In the initial experiments at constant heating rates, the N_2O was also measured by a BIO-RAD FTS 40 FTIR. In the cases of CO_2 in the inlet gas, m/z 44 was assumed to be all CO_2 , and no N_2O measurements were made. In all cases, m/z 28 was corrected for CO fragmentation from CO_2 . No NO_2 was observed.

Whenever NH_3 and O_2 were passed into the mass spectrometer, H_2O and N_2 were observed as products. The ratio of H_2O to N_2 corresponded to NH_3 combustion. Approximately 20% of the NH_3 was burnt in the hot MS source. This side reaction was accounted for by measuring a baseline concentrations of these species before each run.

RESULTS AND DISCUSSION

Nitrogen oxide removal utilizing SCR with NH_3 as the reductant is chemistry which could go through several reactive oxide intermediates, such as N_2O , NO_2 , N_2O_4 , N_2O_3 (6). In this initial study, we make no attempt to study the mechanism(s) of the reactions. We only use the stoichiometry of suspected reactions to substantiate (but not necessarily prove) the overall global reactions. The general global reactions which need to be considered are:



where reaction (1) is a combination of reactions (2) and (3). Potential competing reactions which may be observed under the conditions of these experiments are:

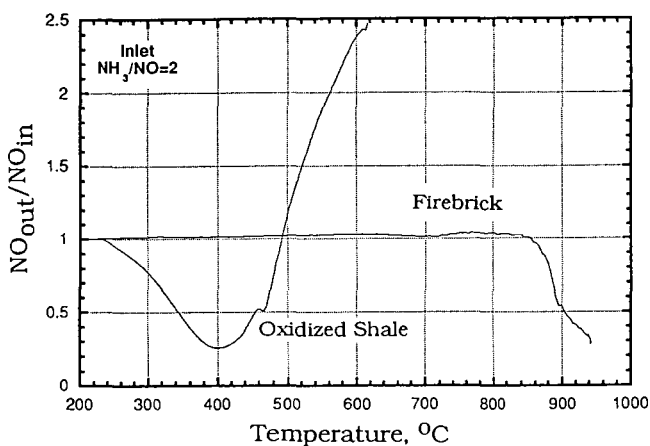
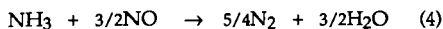


Figure 1. Loss and formation of NO from a mixture of ammonia and NO passed over heated oxidized shale and firebrick (5% O₂, NH₃/NO = 2, rate of heating 10°C/min).

NO Reduction at the Heating Rate of 10°C/min

Oxidized Oil Shale. Oxidized (combusted) Green River oil shale was heated at 10°C/min in a gas mixture of Ar with ~ 5% O₂, 2000 ppm NO, and 4000 ppm NH₃ at a gas residence time of ~ 0.6 sec from 200 to 700°C. Figure 1 shows the results. At 250°C, the NO concentration of the reactor effluent begins to decrease with respect to the NO concentration in the reactor inlet (NO_{out}/NO_{in} < 1.0). This decrease continues to 400°C where a maximum NO removal of 70% is reached. For temperatures above this maximum, NO removal activity steadily decreases. At temperatures above ~ 500°C, there is a net production of NO, which continues to increase the concentration of NO in the reactor effluent with increasing temperature.

The decrease in NO in the reactor effluent at temperatures from 250 to ~ 500°C is probably due to NO reduction by NH₃, mostly by reaction (1). Rough nitrogen balances for N₂ production and NO and NH₃ consumption support this. This behavior is in the temperature range observed for SCR of NO by commercially available V-Ti NO reduction catalysts (3). At temperatures above ~ 500°C, net NO is produced (NO_{out}/NO_{in} > 1). Rough mass balance indicates this

is probably due to ammonia oxidation, reaction (5), and nitrate decomposition (see below). Note at ~ 600°C, a large fraction of NH₃ appears to be converted to NO.

Even without NH₃ as a reducing agent, this lime-bearing sample of burnt shale (see experimental) removed NO from the gas stream at temperatures of ~ 380°C. No N₂ was released, and the amount of oxygen consumed is consistent with the following reaction for the formation of calcium or some other nitrate:



After this shale has been reacted with NO and O₂, heating above 400°C results in the release of NO and O₂, consistent with published data on the thermal stability of some nitrate compounds (7). However, x-ray diffraction did not reveal any nitrates (possibly due to low concentrations).

Firebrick. Figure 1 also shows the behavior of the same gas mixture flowing over firebrick under the same conditions. Obvious is total the lack of NO removal activity until temperatures above 850°C. This is in the temperature range assigned to thermal denox (4). Although not shown, NH₃ over firebrick (with no NO) begins to oxidize at temperatures above 500°C, not yielding any significant amount of NO, but yielding H₂O/N₂ = 3, suggesting reaction (2) is occurring. Full oxidation of NH₃ is seen only at 950°C, where thermal denox is taking place at the same time.

We presume that if the mixture of NO and NH₃ had been heated to 900°C over oxidized (combusted) shale, NO would have decreased to the values observed over firebrick. This prediction is based on the assumption that at high temperatures thermodynamic equilibrium is likely to prevail, and at 900°C, NO remains unstable with respect to N₂ and O₂.

Table 1. Removal of NO over Combusted Oil Shale (Isothermal)

Experiment, #	T, °C	NH ₃ /NO	CO ₂	NO Removal, %	~ Residence Time (sec)
1	365	2.8	No	64	0.6
2	365	0 ^a	No	19	0.6
3	375	2.8	Yes	49	0.6
4	383	2.8	Yes	50	0.6
5	374	0 ^a	Yes	8	0.6
6	385	1.3	Yes	62	1.2
7	402	1.0	Yes	63	1.2
8	385	1.0	Yes	61	1.2

a. No NH₃ in gas stream

NO Reduction at Isothermal Conditions

Figure 1 shows the temperature for maximum NO reduction over oxidized (combusted) shale is 400°C at the 10°C/min heating rate. In efforts to optimize removal conditions and obtain better mass balances, NO removal was performed isothermally over the oxidized (combusted) oil shale. Table 1 lists these results using the shale from the HRS pilot plant (contains 0.3 wt % char).

Oxidized (combusted) shale (Experiment 1). The first experiment listed in the table was carried out with the same gas composition as in the constant heating rate experiments shown in Figure 1. The NO removal is slightly lower than the maximum removal found for the constant heating rate experiment. We do not know the source of this difference, and more experiments are being performed to assess the reason. However, this may be due to the shale bed in the isothermal experiments contained little or no lime preventing NO removal by nitrate formation as a supplement to SCR.

Table 2. Normalized Nitrogen Balances for Removal of NO over Combusted Oil Shale (Isothermal)

Experiment #	<u>Consumed</u>		<u>Produced</u>	<u>Net</u>
	N from NO	N from NH ₃	N as N ₂ *	$\Sigma_{\text{pro}} - \Sigma_{\text{con}}$
1	1.00	1.46	2.58	0.12
2	1.00	0.15	2.09	0.94
3	1.00	1.44	2.44	0.00
4	1.00	1.20	2.34	0.14
5	1.00	0.10	0.11	-0.99
6	1.00	0.85	1.95	0.10
7	1.00	0.94	2.12	0.18
8	1.00	0.81	1.87	0.06

* m/z 28

Overall normalized nitrogen balance of the experiments in Table 1 are shown in Table 2. If all of the NO is consumed by reaction (1) (NO/NH₃/N₂ stoichiometry, 1/1/1; that is one N is released for each NO lost and one N is released for each NH₃ lost), an additional 0.46 moles of N from NH₃ remains to be accounted for by some other reaction. This could be almost all accounted for by the oxidation of NH₃ by reaction (2) which would produce 0.46 moles of N as N₂.

This reaction could be verified by H₂O and O₂ balances. However, O₂ and H₂O balances are complicated by the combustion of char (CH_{0.4}). For example, in experiment 1, the predicted net O₂ loss through the bed (normalized to NO as in the case of Table 2) would be 0.52 from NH₃ combustion and NO decomposition (reactions (1) and (2)) whereas the measured loss in O₂ was 2.5. The predicted H₂O production would be 2.0 but the measured production of H₂O was 2.9. The observed production of CO₂ was ~ 2, accounting for the observed extra O₂ loss. The CO₂ concentration decreased with time, due to the consumption of char. Furthermore, low temperature combustion of char can release CO (m/z 28) which may explain why more N₂ (m/z 28) was seen than can be accounted for by NH₃ and NO loss.

Oxidized (combusted) shale without NH₃ (Experiment 2). The second experiment in Table 1 shows the reaction of NO over the oxidized (combusted) shale in the absence of NH₃ as the reductant. (Very low levels of NH₃ were detected in both the inlet and product streams, probably because of desorption from prior runs, or background correction errors.) Some decrease in the NO concentration in the product effluent compared to the inlet stream does occur without the presence of NH₃. This could be through reaction (3), or by reduction by char. A 2000 ppm concentration of CO₂ is observed indicating char oxidation. A CO content of 200 ppm in the gas stream from the char oxidation chemistry would explain the observed N balance.

Oxidized (combusted) shale with CO₂ (Experiments 3 and 4). To simulate the real combustion stream for the HRS process, ~ 8% CO₂ was added to the reaction gas mixture. The third experiment in Table 1 shows the NO removal with NH₃ present in excess. Although the removal is almost 50%, which demonstrates the oxidized (combusted) oil shale has catalytic properties even with CO₂ in the gas stream, the removal is reduced to 75% of the removal found without CO₂ in the gas stream. (This is even with the reactor temperature 10°C higher.) Raising the reactor temperature from 375°C to 383°C showed only a 1% increase in removal of NO.

Table 2 shows the normalized nitrogen balance for Experiment 3. If reaction (1) is considered as the sole consumer for the NO, 0.44 moles of NH₃ reacted and 0.44 moles of N as N₂ formed remain unaccounted for. However, these remaining quantities can be accounted for by the oxidation of NH₃ by reaction (2). Although exhibiting poorer closure, the normalized nitrogen balance for Experiment 4 shows a similar result. Probably the improved N balance compared to earlier experiments is due to most of the char has been already consumed in previous experiments, so there is less contribution to m/z 28 from CO producing reactions. This is suggested because of 75% of the H₂O produced can be accounted for by NH₃ oxidation in this experiment. Also, the concentration of CO₂ in the exit gas was only 400 ppm compared to nearly 2000 ppm in the earlier experiments 1 and 2.

Oxidized (combusted) shale with CO₂ and without NH₃ (Experiment 5). The CO₂ in the gas stream also appears to have an effect on the ability of the catalyst to remove NO with or without the presence of the NH₃ reductant. Comparing the second and fifth experiments in Table 1 shows the NO removal with CO₂ but no NH₃ in the gas stream is ~ 50% lower than in the case without CO₂ in the stream. This may be due to the absence of char as a reducing agent or due to absorption (see above) instead of catalysis, suggesting the CO₂ is competing with NO for absorption sites on the shale. This will be addressed in detail in another paper.

Effect of Flow Rate and NH₃ to NO ratio on NO Removal (Experiment 6-8). Experiments 6-8 in Table 1 also show NO removal increases significantly when the gas stream residence time (containing CO₂) is doubled to ~ 1.2 sec. These conversions are comparable to the baseline case where no CO₂ is in the gas stream. Because the NH₃ to NO ratio was decreased for this set of experiments, a direct comparison to NO removal at the higher flow rate is not possible. However, these results indicate changing the flow rate (or residence time) is an important variable in maximizing the NO reaction chemistry, particularly when temperature change has an upper limit of ~ 400°C where NO formation (through reaction (5)) begins to compete.

The two experiments (6 and 8) at 385°C reactor temperature and the 1.2 sec residence time show little dependence of NO removal on the NH₃ to NO ratio. This dependence has been studied for a broader range of NH₃ to NO ratios (0 to 2.8) for thermal denox over firebrick. Those results showed a greater difference than seen for NO removal by oxidized oil shale. At 933°C, the firebrick showed for NO_{out}/NO_{in} ~ 0.48, NH₃/NO = 1.0; for NO_{out}/NO_{in} ~ 0.25, NH₃/NO = 1.30.

Table 2 shows for NH₃/NO = 1 (Experiment 8), the amount of NO reacted that can be accounted for by reduction with NH₃ (reaction (1)) is 80%. The source of the consumption of the balance of NO is uncertain. Experiment 5 at the higher gas-flow rate indicates ~ 10% decrease in NO concentration in the gas stream even when NH₃ is not present, probably by reduction by char. However, all the char was probably consumed by the time this experiment was done. Also, lime formation can not take place in the presence of CO₂ at this temperature, so NO consumption by nitrate formation probably does not occur. Reaction (3), though, when applied to

the balance of NO gives excellent N closure. Further experiments are being conducted to clarify this.

CONCLUSIONS

Oxidized (combusted) oil shale from the HRS process exhibits catalytic activity for the removal of NO from laboratory gas streams using NH_3 as the reductant. The activity and conditions have not been optimized, but typical NO removal is 60+% at a 1.2 sec gas residence time, a reactor temperature range of 380 to 400°C, and for a gas containing ~ 2000 ppm NO, 2000 ppm NH_3 , and 8% CO_2 . Temperature limitations potentially due to competing NH_3 oxidation suggest residence time is the important variable to study for improving removal of NO from flue gas. Optimizing this process variable, as well as application to actual retort combustor gas streams will be addressed in a later paper.

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